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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Roger Lok, et al

SILVER HALIDE ELEMENTS  
CONTAINING ACTIVATED  
PRECURSORS TO THIOCYANATO  
STABILIZERS

Serial No. 10/727,833

Filed 04 December 2003

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA. 22313-1450

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Group Art Unit: 1752

Examiner: LE, Hoa Van

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*Frieda Grinnell*  
Frieda Grinnell

*July 27, 2005*  
Date

**DECLARATION UNDER 37 CFR 1.132**

I, Paul A. Zielinski, hereby declare as follows:

1. I am an applicant and co-inventor of the subject matter claimed and described in the above-identified U.S. patent application

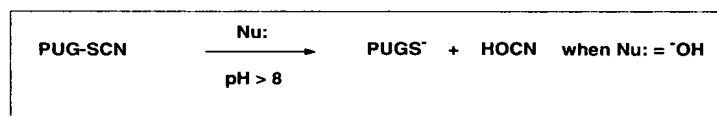
2. I received my Bachelor of Science (Chemistry) from the University of Illinois-Chicago in 1970 and my Master of Science (Organic Chemistry) from the Rochester Institute of Technology in 1976. I have been employed by the Eastman Kodak Company for over 35 years. I am currently, and have been for a number of years, a Research Associate in the Research Laboratories of the Eastman Kodak Company. My career has been devoted to organic chemistry as it pertains to imaging science and materials. I am co inventor of 19 US Patents plus numerous other counterpart patents granted by other countries.

3. I have read and understand the Office Action dated March 22, 2005 and the art cited against the above identified U.S. Patent Application.

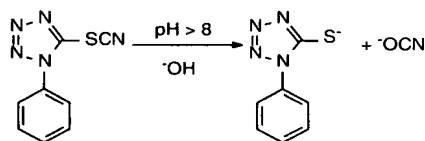
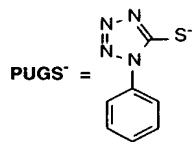
4. The materials described in Stauffer are inorganic complexes. When these inorganic complexes are incorporated into a silver halide emulsion, anionic thiocyanate anion ( $\text{SCN}^-$ ) is released from the ionic palladium complex. The released anionic thiocyanate anion ( $\text{SCN}^-$ ) forms a strong complex with silver. (Please see "The Theory of The Photographic Process" 4<sup>th</sup> Edition, T.H. James (Editor), pages 9 and 446.)

5. The materials in the invention are organic thiocyanato compounds. They are covalent organic compounds. The sulfur of the thiocyanato moiety is covalently bound to the PUG moiety. The inventive materials do not release thiocyanate anion ( $\text{SCN}^-$ ). The inventive materials, when treated in the development step at  $\text{pH} > 8$ , release PUGS.

6. The inventive organic thiocyanato compounds can be considered blocked mercaptans. They are stable at emulsion  $\text{pH} < 7$  but rapidly release desired photographically useful mercaptan groups ( $\text{PUGS}^-$ ) during the development step at  $\text{pH}$  preferably  $> 8$ , and more preferably  $> 9$ . In our work:



For example, in thiocyanato compound (1):



In this inventive compound, the nucleophile ( $\text{OH}^-$ ) attacks the carbon atom of the  $-\text{SCN}$  group. The driving forces are the release of the photographically useful 1-

aryl-5-mercaptopotetrazole (PUGS<sup>-</sup>) and HOCN. Photographic results are consistent with the release of the photographically useful mercaptan (PUGS<sup>-</sup>). Mechanistic studies (MS-HPLC) at Eastman Kodak Company confirm that Compound 1 and other organic thiocyanato compounds release the photographically useful mercaptan (PUGS<sup>-</sup>) when treated at pH > 8.

7. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date:

July 22, 2005

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TABLE 1.5  
Dissociation Constants of Homogeneous Silver Complexes in Water at Room Temperature

Ligand	$pK_{sp}$	$pK_{11}$	$pK_{12}$	$pK_{13}$	$pK_{14}$
$Cl^-$	9.75	3.3	5.25	5.7	5.4
$Br^-$	12.31	4.5	7.4	8.5	9.0
$I^-$	16.09	7.5	11.6	14	~15
$CN^-$	15.8	~9	20.7	21.9	21
$SCN^-$	11.97	4-5	~8	10.3	10.9
$SeCN^-$	15.4	—	11.0	13.8	
$SO_3^{2-}$	13.8	5.5	8.7	8.9	
$SO_4^{2-}$	4.9				
$S_2O_3^{2-}$		~9	13.3	13.9	
Thiourea <sup>a</sup>		7.3	10.6	12.8	13.7
$S^{2-}$	49.1				
$HS^-$		13.2	17.2		
$Se^{2-}$	63.7				
$OH^-$	7.71	2.0	4.0		
$NH_3$		3.3	7.2		
Aliphatic primary amines		3.0-3.5	6.8-7.5		
Aliphatic secondary amines		~3	5.3-6.4		
Aliphatic tertiary amines		~2.6	3.6-4.6		
Diethylenetriamine		6.1			
1-Ethylenediamine		5.0	7.8		
1,2,3-Triaminopropane		5.6			
Triaminotriethylamine		7.8			
Triethylenetetramine		7.7			
Ethylenediaminetetraacetate (EDTA)		7.0			
Piperidine		3.0	6.5		
Pyridine <sup>b</sup>		2.0	4.2		
Imidazole <sup>c</sup>		3.5	6.9		
Ethanolamine		3.2	6.8		
Triethanolamine <sup>d</sup>		2.3	~4		
$\alpha$ -Amino acids without complexing residue on the side chain		3.5-3.7	7.0-7.2		
Arginine		3.5	~8		
Cysteine		5.2	18.2		
Histidine (neutral medium)		—	7.5		
(high pH)		7.3	8.9		
Methionine (low pH)		3.2	5.7		
$\omega$ -1-3 to 1-6- <i>n</i> -Amino acids		3.4-3.7	7.5-7.8		
Monothioglycol	19.6	13.2	17.8		
Thiosemicarbazide				12.8	
1-Phenyl-5-mercaptopotetrazole	16.2	10.9	13.6	15.3	

<sup>a</sup> For thio- and seleno-alkenes, see reference 59.

<sup>b</sup> For pyridine derivatives, see reference 60.

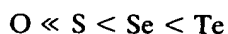
<sup>c</sup> For substituted imidazoles, see reference 61.

<sup>d</sup> For other amino alcohols; see reference 62.

In spite of these uncertainties, it is possible to draw general relations in homologous series. For instance, with halide and pseudo-halide ions, the order of increasing stability is



Similar relations have been established for the silver complexes formed by ether type compounds containing group VI donor atoms and by tertiary ligands with group V donor atoms, their stability changing in the following sequences



Mixed complexes (Table 1.6) always coexist in solution with homogeneous complexes formed by the silver ions with the two ligands separately. When the  $pK$  of the homogeneous compounds are accurately known, the determination of the constants of the mixed complexes requires the solution of systems of equations involving six unknown parameters. The problem is more complicated when one or several homogeneous complexes are poorly known and the difficulties encountered explain why some mixed complexes that, owing to the stepwise formation, certainly exist in solution, have not been detected. Nevertheless, not all of the blanks in Table 1.6 are due to a lack

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An aqueous 10% solution of thiourea can dissolve 8.3 g of AgCl, 18.7 g of AgBr, and 7.9 g of AgI per liter.<sup>53</sup> When thiourea is added to a silver nitrate solution the precipitate that is first formed dissolves when the mole ratio of thiourea to silver is approximately 3:1. Fyfe<sup>54</sup> found the stability constant under these conditions to be 13.05. The heats of formation of the Tu complexes suggest that the first ligand forms an S—Ag bond, whereas further ligands bond through N.<sup>55</sup>

Bruenner<sup>56</sup> described the stabilizing properties of thiourea and a number of its derivatives. The prime difficulty, as originally observed by Bogisch, is that the complexes degrade to silver sulfide as soon as they are made alkaline. Ethylenethiourea was more stable in this respect but was slower in fixing. As a result, contamination of unprocessed material with traces of thiourea will cause fog in an alkaline developer. Another difficulty is the strongly corrosive action of thiourea on silver in the presence of oxygen. Selenium- and gold-toning decrease the attack on the image. Like several other thiol compounds, for example, thiosalicylic acid, though not cysteine, thiourea has a softening action on gelatin and the stabilized emulsion is very tacky. Bruenner reported that the condensation products of thiourea and formaldehyde were nontacky but otherwise comparable to thiourea in stabilizing characteristics.

### 3. THIOCYANATE

The most widely applied stabilizing agent has been ammonium thiocyanate, which was introduced as a fixing agent in 1862.<sup>57</sup> At high concentrations this agent fixes much more rapidly than the thiosulfate.<sup>27,34</sup>

Thiocyanate-silver complexes are stable and do not degenerate to silver sulfide on being made alkaline though, in the case of the ammonium salt, ammonia would be lost at an elevated pH. Silver thiocyanate, AgSCN, is a white salt almost as insoluble as silver bromide. It dissolves readily in excess thiocyanate to form a series of complexes with two or more SCN<sup>-</sup> ions per silver ion (Chapter 1, Table 1.5). Because of the insolubility of silver thiocyanate and the relatively low stability constant of the dithiocyanate, that is, between four and five orders of magnitude less than the dithiosulfate, thiocyanate-fixed emulsions cannot be washed without maintaining an adequate concentration of free thiocyanate or another complexing agent, for example, thiosulfate.<sup>58</sup>

Blyumberg<sup>59</sup> and Kawasaki<sup>27,60</sup> found the rate of clearing of initially dry emulsion to reach a maximum (see Figure 15.8) and then decrease, whereas Kulane and Hähnel<sup>24</sup> found an increase in rate of solution of solid AgCl and AgBr up to 9 M ammonium thiocyanate with no indication of a decrease, and their

experiments with dry emulsion showed no decrease up to 5 M. The data of the latter authors show the rate of solution from the solid and the emulsion to be related to the concentration of ammonium thiocyanate as  $R = k_1[\text{NH}_4\text{SCN}]^{1.9-2.3}$ . Sahyun<sup>61</sup> found the rate to vary as  $R = k_2[\text{NH}_4\text{SCN}]^3 + d$  and presumed that this showed that the formation of the  $\text{Ag}(\text{SCN})_3^{2-}$  complex ion was rate determining. By the same argument, however, the earlier data would indicate the formation of  $\text{Ag}(\text{SCN})_2^-$  as being the important step. Both these studies agree in showing the course of fixation to be of first order, the rate being proportional to the concentration of residual silver within the emulsion. In both cases the methods of analysis did not distinguish between undissolved silver halide and complexed silver. Interestingly, the course of fixation as measured photometrically by Blyumberg and coworkers, on the assumption that the density of the emulsion was proportional to silver halide concentration, had the same accelerating shape as that found by Sheppard and Mees for thiosulfate (Section I-B.3).

Figure 15.8 shows that, at higher concentrations, the rate of fixing in ammonium thiocyanate solutions greatly exceeds the rates in ammonium and sodium thiosulfate solutions. This difference in the behavior of highly concentrated thiocyanate and thiosulfate solutions can be associated with the free swelling<sup>27b</sup> of a dry emulsion in the former and its very restricted swelling in the latter. Blyumberg and coworkers<sup>59</sup> found ammonium and potassium thiocyanates to be comparable in fixing rate and both much faster than the sodium salt. The advantage decreased with increasing concentration and increasing temperature, Table 15.3. The data for the temperature coefficients for the dissolution of silver halides in thiocyanates are varied. Sahyun found the apparent activation energies (12–38°C) to range from 0 to 8.3 kcal mole<sup>-1</sup> for sodium thiocyanate, whereas Blyumberg and coworkers found the apparent activation energy for the dissolution of AgBr by ammonium thiocyanate to increase with temperature from a slightly negative value of -1.3 at 20°C to 9.8 kcal mole<sup>-1</sup> at 60°C.

Concentrated thiocyanate solutions, and patches of dried-down thiocyanates, undergo a photocatalyzed degradation<sup>62</sup> to give a bright yellow product of the character of polythiocyanogen. In direct sunlight there is a critical concentration near 1.5 M, below which solutions of ammonium thiocyanate do not discolor (Figure 15.12) and the same value is obtained for dry patches of ammonium thiocyanate on paper if the salt is assumed to be dispersed uniformly through the body of the cellulose fiber. One proposal for stabilizing thiocyanate-treated prints involves the reduction of the thiocyanate concentration by a final rinse in a dilute, for example, 3.5% solution of thiocyanate, or a